



Synthesis of pyridine and methylpyridines over zeolite catalysts

Nellya Gennadievna Grigor'eva ·

Nadezhda Alexandrovna Filippova ·

Marina Ivanovna Tselyutina · Boris Ivanovich Kutepov

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Abstract The synthesis of pyridines has been performed by a multi-component reaction of ethanol, formaldehyde, and ammonia in the presence of H-Beta, H-ZSM-12, and H-ZSM-5 zeolite catalysts. The maximum activity in the reaction is revealed by H-Beta zeolite; the conversion of ethanol induced by it reached 70% (400 °C, 2 h⁻¹). The main products of the reaction in the presence of H-Beta and H-ZSM-5 zeolites are pyridine and picolines; on H-ZSM-12 picolines and lutidines. Thus, the results of the studying the effect of reaction parameters are showed that the yield of lutidine and heavy products increases with the increase of the temperature (from 200 to 400 °C) and the decrease of the weight hourly space velocity (from 10 to 2 h⁻¹).

Keywords Pyridine · Picolines · Lutidines · Zeolites · Multi-component reaction

Introduction

Pyridine and substituted pyridines are the important intermediates for the synthesis of pharmaceuticals, herbicides, metal corrosion inhibitors, rubber vulcanization accelerators, and conventional ligands for the chemical assembly of coordination compounds [1–4].

The first industrial method for the pyridine production is the separation from the coal-tar [5] where the content of it is less than 0.01 %.

To date the major industrial processes for the synthesis of pyridine and methylpyridines use gas phase condensation of carbonyl compounds with ammonia induced by the aluminosilicates promoted with metals, namely, Ni, Cr, Cd, Zn, Th. The pyridine yield amounts 40–60 %, and a sizeable amount of by-products is formed [3, 6].

The successful application of zeolite catalysts in the processes of acid–base catalysis such as isomerization, amination, aromatics transalkylation, oligomerization, catalytic cracking, and others has opened up the new possibilities for the synthesis of N-heterocyclic compounds.

The synthesis of pyridine and alkylpyridines by a reaction of aldehydes and ketones with ammonia over MOR, FAU, BEA zeolites [7–10] and ZSM-5 zeolite modified by various metal ions [11–18] is described.

It has been determined [19–21] that the pore size HA, HX, HY zeolites had insignificantly effect on selectivity towards pyridine formation. At the same time, the H-ZSM-5 zeolite and silicalite (SiO₂/Al₂O₃ = 30–120) promoted by Pt(II), Ti(I), Zn (II) or Co (II), have the pore diameter are nearly identical to pyridine molecule and it allows to achieve high selectivity of pyridine.

Liu et al. [22] reported that the yield of pyridine was achieved 50 % using Co-ZSM-5 zeolite catalyst.

Kulkarni and Subrahmanyam [23] described the synthesis of pyridines from acetone, formaldehyde and methanol with ammonia over ZSM-5 (SiO₂/Al₂O₃ = 30, 150, 280) zeolite promoted by Pb, W. The main reaction products are 2-picoline (30–47 %) and 2,6-lutidine (15–35 %).

Van der Gaag et al. [24] proposed a method for the synthesis of pyridines from ethanol and ammonia in the presence of oxygen over ZSM-5 zeolite promoted by Cd, Co or Fe and H-Mor, H-Y zeolites. It is shown that with the increasing of the SiO₂/Al₂O₃ ratios (from 12 to 130) the selectivity of pyridine increases and amount to 23–47 %.

N. G. Grigor'eva (✉) · N. A. Filippova ·
M. I. Tselyutina · B. I. Kutepov
Federal State Budget Institution of Science, Institute of
Petrochemistry and Catalysis Russian Academy of Sciences, 141
prosp. Oktyabrya, 450075 Ufa, Russian Federation
e-mail: ngg-ink@mail.ru

Ferrum-modified ZSM-5 zeolite showed high activity and selectivity to pyridine. In the case of using H-Mor or H-Y zeolite carbon dioxide and ethylene are major products.

Synthesis of pyridines from ethanol, formaldehyde and ammonia has been a subject of great interest [25]. This reaction was carried out for the first time by Indian scientists over various ZSM-5 catalysts. Zeolite catalysts of the other framework were not studied in this reaction.

In this paper, the multi-component reaction of ethanol with formaldehyde and ammonia under the action of different zeolite catalysts, such as H-Beta (BEA), H-ZSM-12 (MTW), H-ZSM-5 (MFI) was carried out.

Experimental

Reagents and catalysts

The ethanol (95 %), aqueous solutions of formaldehyde (37 %) and ammonia (28 %) was used with no additional purification.

The Beta zeolite (the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 18) and ZSM-12 zeolite ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 34$) were supplied by OJSC “Angarsk Plant of Catalysts and Organic Synthesis” in NH_4 -form. Zeolite samples were converted into the H-form by calcining them in the atmosphere of air at the temperature of 540 °C for 3 h.

H-ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$) zeolite was obtained from OJSC “Novosibirsk Plant of Chemical Concentrates”.

The zeolite samples were calcined in the atmosphere of air for 3–4 h at 540 °C.

The catalysts were characterized by the X-Ray Phase (XRP) and X-Ray Diffraction (XRD). Studies, the Low Temperature Nitrogen Adsorption, and the Temperature Programmed Desorption of ammonia (TPD NH_3) were described in [26–29].

General procedure for synthesis of pyridines

The reaction of ethanol with formaldehyde and ammonia was conducted in a tubular, down-flow Pyrex reactor with 20 mm internal diameter at the temperature of 200–400 °C and the weight hourly space velocity (WHSV) within the range of 0.5–10 h^{-1} . The molar ratio of ethanol/formaldehyde/ammonia varies within the range of 1.0/0.4–1.1/1.5. The amount of the catalysts taken for every reaction was 0.4 g. The reaction mixture was fed from the top using a micro-pump. The product was collected at the bottom and cooled using ice-cold water.

The reaction products were analyzed by means of the gas–liquid chromatography technique using the chromatograph with the flame ionization detector (SE-30 phase, the glass capillary column of 25 m length; the temperature of

analysis 50–280 °C; the programmed heating gradient of 8 °C/min; the detector temperature of 250 °C; the evaporator temperature of 300 °C; the flow rate of the helium carrier gas of 30 cm^3/min).

High resolution mass spectra are recorded using the Fisons company instrument, its chromatograph being equipped with the 50 m DB-560 capillary quartz column (50 m).

The products were identified by comparing the mass spectra and chromatographic behavior of the separated and reference products (pyridine, picolines, and lutidines).

Result and discussion

According to the XRP, XRD data, and the adsorption measurements, all the zeolite samples tested have the crystallinity degree close to 100 %.

The zeolites investigated in this work belong to different structural types, namely, BEA, MTW, MFI and are differing in the crystal structure, the framework atom ratio, and acidic properties.

H-Beta zeolite has possessed the most wide rectilinear channels, bordered by the 12-ring [30]; the diameter of ZSM-5 and ZSM-12 zeolite channels were the most tight ones.

Since the catalytically active centers in zeolites are basically located inside the channels, the active sites of H-Beta zeolite possessing the most open crystalline structure with the widest pores will be obviously more accessible to the reactive molecules.

In the acidic spectra of zeolite catalysts obtained by the TPD NH_3 method, there are two peaks characterizing the “weak” acid sites with the temperature maximum T_{max} in the temperature range of 100–350 °C and the “strong” acid sites with the temperature maximum T_{max} in the temperature range over 350 °C (see Table 1).

The total acidity of the zeolites followed the order: H-Beta > H-ZSM-5 > H-ZSM-12, as given in Table 1. Chemical transformations on zeolites occur primarily with the acid sites; their concentration decreases in the following series: H-Beta > H-ZSM-5 > H-ZSM-12. The strength of the “strong” acid sites in the zeolite studied was evaluated by the shift of the high temperature maximum T_{II} in the thermal desorption patterns appeared to be approximately the same.

We have found that under the action of H-Beta, H-ZSM-5, and H-ZSM-12 zeolite catalysts ethanol interacts with formaldehyde and ammonia yielding pyridine, picolines (2-methylpyridine, 3-methylpyridine, 4-methylpyridine), lutidines (dimethyl-pyridines), and more “heavy” compounds as compared to dimethylpyridines (see Scheme 1).

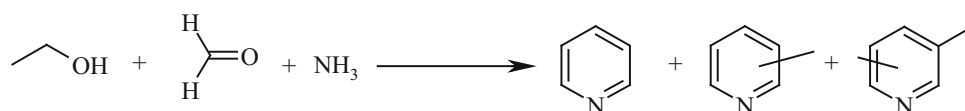
The activity of catalysts evaluated by the degree of ethanol conversion reaches its maximum on the H-Beta

Table 1 The characteristics of zeolite catalysts

Catalyst	Structure	Channels diameter (Å)	Si/Al ratio	Degree of crystallinity (%)	Equilibrium adsorption capacity*		Acidic properties			
					H ₂ O	C ₆ H ₆	T_{\max} (°C)		Concentration of the acid sites (mmol g ⁻¹)	
							I	II	C _I	C _{II}
H-Beta	12-Rings	6.6 × 6.7 and 5.6 × 5.6	18	100	0.12	0.32	280	450	520	310
H-ZSM-12	12-Rings	5.6 × 6.0	34	100	0.07	0.23	300	450	220	90
H-ZSM-5	10-Rings	5.1 × 5.5 and 5.3 × 5.6	28	100	0.05	0.20	250	450	210	280

C_I and C_{II} denote the concentration of «weak», «strong» acid sites

* 20 °C and P/Ps = 0.8

Scheme 1 Synthesis of pyridines

zeolite catalyst and decreases going to pentasil-zeolites (H-ZSM-5 and H-ZSM-12) (see Table 2).

Main reaction products in the presence of H-Beta zeolite are pyridine and methylpyridines formed in the approximately equal quantities, i.e., 44 and 46 %. The content of dimethylpyridines and “heavy” products is negligible—6 and 4 % (see Table 2). So far as the selectivity of the pyridine formation is concerned, close results are obtained on H-ZSM-5 zeolite: the pyridine/picoline ratio of $\approx 1/1$; the content of lutidines is for practical purposes, the same as on the H-Beta catalyst. It is worth to mention the higher selectivity of the “heavy-products” formation as compared to H-Beta zeolite. A distinction of the H-ZSM-12 zeolite catalyst is the higher content of methyl- and dimethylpyridines in the reaction products amounting about 77 % of the pyridine total. The pyridine/picolines/lutidines ratio is 1:2.5:0.9.

Among the picolines obtained on H-ZSM-5, H-ZSM-12, and H-Beta zeolites prevails 3-methylpyridine (see Table 2). In the lutidine composition, 3,5-dimethylpyridine is the major isomer, its quantity exceeding 90 %.

To explain the results obtained let us refer to the characteristics of the porous structure of zeolite catalysts and their acidic properties (see Table 1).

The comparison of acidic properties and characteristics of the porous structure of the studied zeolites with their activity in the reaction of ethanol with formaldehyde and ammonia shows that the higher activity of H-Beta zeolite as compared to H-ZSM-5 and H-ZSM-12 pentasils is defined both by the easier accessibility of the acid sites to the reactive molecules and by the higher concentration of the acid sites.

The selectivity of the pyridine formation is probably defined to the most extent by the structural characteristics of zeolite catalysts. Therefore, on the H-Beta zeolite possessing the widest channels in the series of the catalysts studied all three methylpyridine isomers are formed in sizeable quantities, whereas on the more narrow-porous H-ZSM-5 and H-ZSM-12 zeolites 3-methylpyridine is predominantly formed. The effect of the same factor (the smaller pore diameter) may be also attributed to the fact that the content of dimethylpyridines is higher on the products obtained on H-ZSM-5 and H-ZSM-12 zeolite catalysts. The bulky lutidine molecules are likely to be formed not in the zeolite channels, but on the superficial acid sites.

In the presence of the most active zeolite catalysts, the H-Beta catalyst, we studied the effect of the reaction

Table 2 Effect of the zeolite framework types on the conversion of ethanol (K) and on the selectivity of the pyridines formation (300 °C, 7 h⁻¹, C₂H₅OH/CH₂O/NH₃ molar ratio of 1.0/0.8/1.5)

Catalyst	K (%)	Selectivity (%)					
		Pyridine	2-Picoline	3-Picolines	4-Picolines	Lutidines	«Heavy-products»
H-Beta	40	44	9	22	15	6	4
H-ZSM-5	30	42	1	37	5	7	8
H-ZSM-12	24	21	4	40	8	19	8

Table 3 The effect of temperature on the conversion of ethanol (K) and on the selectivity of the pyridines formation (H-Beta catalyst, C₂H₅OH/CH₂O/NH₃ molar ratio = 1.0/0.8/1.5; WHSV = 2 h⁻¹)

T (°C)	K (%)	Selectivity (%)					
		Pyridine	2-Picoline	3-Picoline	4-Picoline	Lutidines	«Heavy-products»
200	40	49	4	6	31	4	6
250	43	45	9	12	22	5	7
300	59	42	8	16	19	7	8
350	66	39	3	32	5	11	10
400	70	27	2	32	2	20	17

Table 4 The effect of the WHSV on the conversion of ethanol and on the selectivity of the pyridines formation in the presence of H-Beta catalyst (300 °C; C₂H₅OH/CH₂O/NH₃ molar ratio of 1.0/0.8/1.5)

WHSV (h ⁻¹)	K (%)	Selectivity (%)					
		Pyridine	2-Picoline	3-Picoline	4-Picoline	Lutidines	«Heavy-products»
0.5	63	38	5	16	18	12	10
2	59	42	8	16	19	7	8
4	48	42	9	22	14	7	6
7	40	44	9	22	15	6	4
10	36	49	10	19	15	4	3

Table 5 Effect of the reagent molar ratio on the conversion of ethanol and on the selectivity of pyridines formation in the presence of H-Beta zeolite catalyst (at T = 300 °C and WHSV = 7 h⁻¹)

Feed	Molar ratio	K (%)	Selectivity (%)					
			Pyridine	2-Picoline	3-Picoline	4-Picoline	Lutidines	«Heavy-products»
Ethanol-formaldehyde-ammonia	1.0/0.39/1.5	44	33	3	40	8	14	2
	1.0/0.53/1.5	41	35	5	37	11	10	2
	1.0/0.80/1.5	40	44	9	22	15	6	4
	1.0/1.07/1.5	30	48	8	20	16	5	3

parameters, namely, the temperature, weight hourly space velocity (WHSV), reagent molar ratio on the conversion of ethanol and on the composition of pyridines formed as a result of the interaction of ethanol with formaldehyde and ammonia.

As it follows from the data given in Table 3 the conversion of ethanol grows with the rise of temperature.

In the process, the selectivity of the pyridine formation decreases by almost half and dimethylpyridines—increases by five times. The total selectivity of the picolines formation is changed slightly—within the range of 41–36 %, while in the composition of isomers noticeable changes occur. The content of 3-methylpyridine increases with the increase of the temperature and the amount of 2- and 4-methylpyridines decreases. The content of “heavy-products” increases from 6 % (200 °C) to 17 % (400 °C),

which is connected, apparently, with the increase in the rate of side reactions.

The influence of the WHSV on the conversion of ethanol and on the selectivity of the reaction products is depicted in Table 4.

With the increase of WHSV, the contact time between the active site and reactant molecules decreased and correspondingly the conversion of ethanol decreased from 63 % at 0.5 h⁻¹ to 36 % at 10 h⁻¹. In the process, the content of pyridine and picolines in the reaction mixture increases slightly (11 and 7 %, respectively) and the amount of lutidine and “heavy” products decreases.

During the studies of the effect of the reagent molar ratio of ethanol, formaldehyde and ammonia on the conversion of ethanol and the selectivity of the pyridines formation, it is indicated that with the increase of

formaldehyde in the feed (from 0.39 to 1.07 mol) the conversion of the alcohol is reduced (Table 5).

The most selective formation of 3-methylpyridine with up to 40 % yield is possible at the minimum formaldehyde content (the ratio ethanol/formaldehyde/ammonia equals 1/0.39/1.5). As the formaldehyde content increases (1.0/1.07/1.5), the selectivity of pyridine formation increases from 33 to 50 %, and the selectivity of dimethylpyridine formation decreases from 14 to 5 %.

The revealed dependence of the higher methylpyridine yield on the lower amount of formaldehyde in the raw feed is associated with the reaction mechanism proposed in the publications [25, 31]. The main stages of the reaction between ethanol, formaldehyde, and ammonia could be illustrated by the following scheme (see Scheme 2):

It is supposed that imine is the initial product of the reaction; it is formed as a result of the interaction of ammonia with ethanol and acetaldehyde. The latter in its turn is a product of the reaction between alcohol and formaldehyde. The condensation of the formed imine and formaldehyde followed by the cyclization and aromatization result in the formation of pyridine. The condensation of imine without formaldehyde gives methylpyridines.

Conclusion

Thus, the study of the catalytic properties of different zeolites in the multi-component reaction of ethanol with formaldehyde and ammonia has established H-Beta zeolite to be the most active in the synthesis of pyridines; the

conversion of ethanol on it reaches 70 % (at 400 °C and 2 h⁻¹).

The high catalytic activity of H-Beta zeolite is stipulated both by the presence of a significant number of “strong” acid sites in it and by the specifics of the framework structure that provides free access of the reagents to the active sites of the catalyst.

Increasing the temperature from 200 to 400 °C, the decrease in the volume flow rate from 10 to 0.5 h⁻¹, and an increase in the formaldehyde content in the raw feed have been found to increase the conversion of ethanol on H-Beta zeolite.

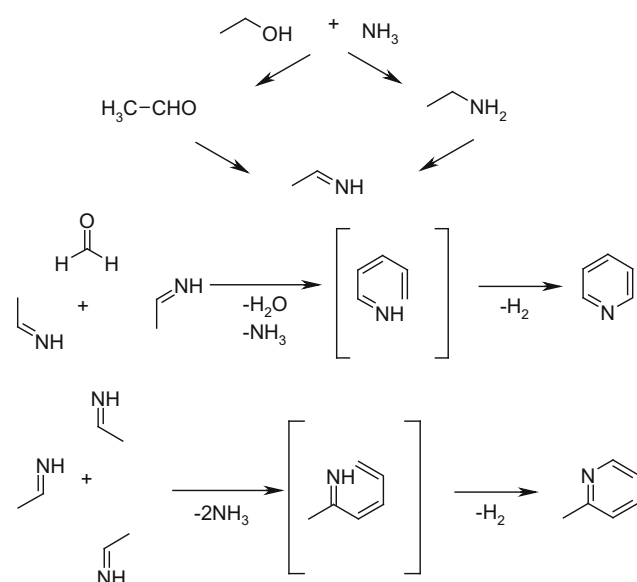
The selectivity of the pyridine formation reaches its maximum of 49 % at 200 °C and 2 h⁻¹. The elevation of temperature, the reduced volume flow rate and formaldehyde concentration in the raw mix result in a higher quantity of methylpyridines and “heavy” compounds in the reaction product composition.

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Scheme 2 Possible reaction mechanism for the formation of pyridine and picolines

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